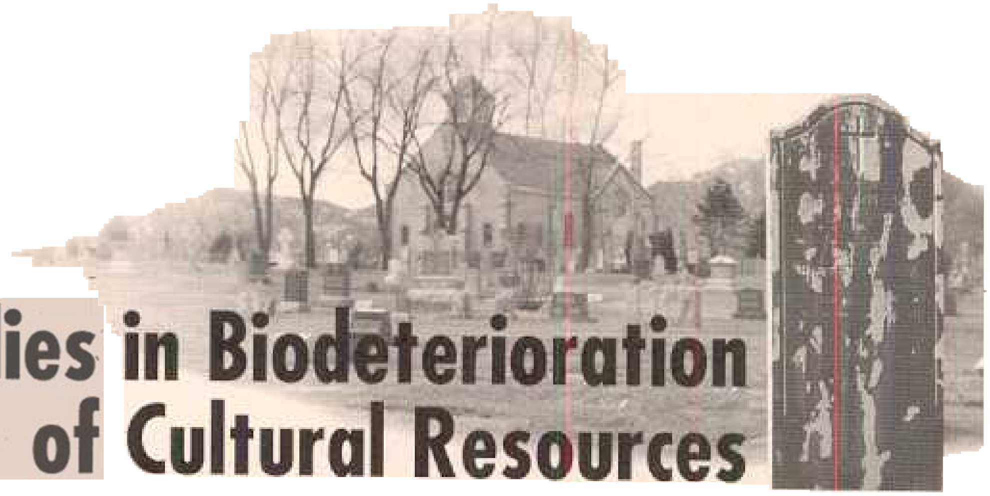
NCPTT NOTES

National Center for Preservation Technology and Training

UNITED STATES DEPARTMENT OF THE INTERIOR • NATIONAL PARK SERVICE

JANUARY 1998

NUMBER 22



Studies in Biodeterioration of Cultural Resources

Outdoor cultural resources — such as historic buildings, tombstones, monuments and sculpture — are under attack by man-made and natural threats. Air pollutants affect works of art in outdoor and indoor environments. Grafitti is rampant in urban settings. Erosion from rain and wind slowly changes outdoor sculpture. Corrosion obscures bronze details once crisply modeled by an artist's hands. And in the midst of these threats is biodeterioration.

Biodeterioration of cultural resources is damage due to the growth of organisms, from microorganisms to higher plants, on the surface of an object. Biological agents of damage can range from colorful lichens to creeping vines. Microorganisms, including bacteria that feed on air pollutants, may cause damage on its surface. Growth of organisms on stone can cause two main types of damage: mechanical damage by the penetration of roots and hyphae, and chemical damage by the secretion of acids capable of chelating to metal ions found in stone.

NCPTT's Materials Research Program recognizes the importance of studying the effects of biodeterioration on masonry. New studies on damage caused by microorganisms, particularly bacteria, are crucial to an overall understanding of stone decay.

In recent years, deterioration of stone buildings and monuments by biodeterioration is a new research focus. As reported in the November 1996 issue of *New Scientist*, leading experts believe that biodeterioration is on the increase, fueled by pollution. While there is a correlation between pollution and observed

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Editor
Mary F. Striegel

Publications Manager
Sarah B. Luster

Contributors
Fran Gale
Mark Gilberg
Melinda A. Hamilton
Rakesh Kumar
Ralph Mitchell
Lee O. Nelson
John Robbins
Robert D. Rogers

Copy Editor
Sara Burroughs

Address
NCPTT
NSU Box 5682
Natchitoches, LA 71497

Telephone
318/357-6464

Facsimile
318/357-6421

Electronic mail
NCPTT@alpha.nsula.edu

Gopher
gopher.ncptt.nps.gov

World Wide Web
http://www.cr.nps.gov/ncptt/

Fax-on-demand
318/357-3214

Newsletter Design
Terra Incognita
Interactive Media
www.terraincognita.com

NCPTT Notes is published by the National Park Service's National Center for Preservation Technology and Training. The mail list for *NCPTT Notes* is subject to request under the Freedom of Information Act. Persons or organizations not wanting to have mail list information disclosed should unsubscribe.

Comments and items of interest for the next newsletter should be sent to NCPTT's publications manager, Sarah B. Luster.

Biodeterioration of stone: What do we know?

Our understanding of the interaction between biological agents and stone materials has increased greatly in the last three decades. This is due to a systematic multidisciplinary approach to the study of stone deterioration.

Biodeterioration — which refers to undesirable changes in a material caused by living organisms — is a complex phenomenon that occurs in conjunction with other causes of decay. The alteration of stone monuments and sculptures by living organisms usually is indicative of an advanced state of deterioration — but because the phenomenology of this decay is similar to other physical and chemical causes, it has not been possible to distinguish the extent of decay caused by biological agents from decay caused by physical and chemical processes. Although the effects of environmental factors are widely recognized, significant debate continues among conservators about biological processes' contribution to stone deterioration.

It is obvious that higher plants cause significant destruction to monuments and their structural stability. Damage caused by microorganisms, on the other hand, is not yet clearly defined or understood.

Biodeterioration research has focused chiefly on bacteria, algae, fungi and lichens; mosses and liverworts have received comparatively less attention because their impact on stone has been considered primarily aesthetic.

The action of bacteria on stone substrates is rather unclear. Large bacterial populations have been detected on weathered stone surfaces, whereas they are only minimally present on unweathered stone surfaces. It is, however, difficult to evaluate whether such observations indicate that bacteria are primarily responsible for stone decay or whether weathered surfaces merely provide a more suitable habitat for bacterial growth. Considerable ambiguities also persist in studies on stone deterioration by cyanobacteria and algae: The only thing that is clear is that these organisms cause discoloration of stone surfaces.

Stone deterioration due to fungi largely depends on the

Studies in biodeterioration

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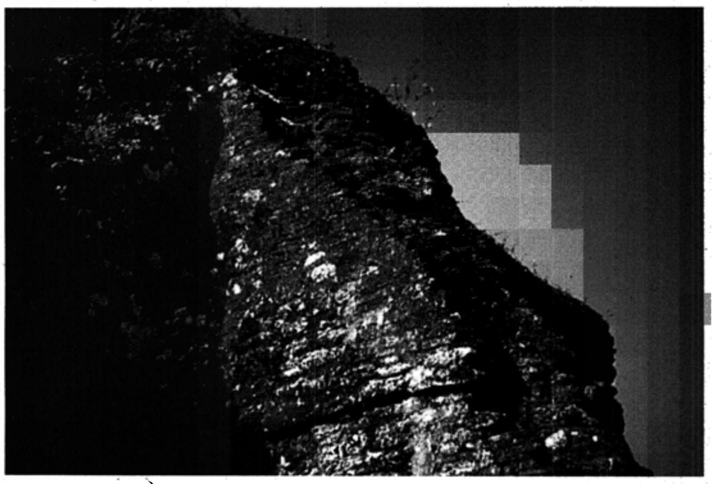
deterioration, the role that microorganisms play has not been fully understood because many other factors also play a role.

NCPTT's Materials Research Program is active in biodeterioration research. A 1997 PTTGrants program award to Dr. Ralph Mitchell at Harvard University supports studies of the interaction between natural microflora and pollutants on limestone. Dr. Mitchell's research will enhance our understanding of the role of microorganisms and their interaction with pollutants in the process of stone deterioration. With this knowledge, more effective remedial treatments to prevent deterioration of historic buildings and monuments can be developed.

This issue of *Notes* includes three articles on biodeterioration of cultural resources. Dr. Rakesh Kumar presents an overview of our current understanding of biodeterioration on stone. Dr. Ralph Mitchell reports on the recent course, "Biodeterioration and the Preservation of Cultural Artifacts," held in Turin, Italy. Microbially influenced deterioration of concrete is discussed by Dr. Robert Rogers and his research colleagues.

NCPTT's Materials Research Program continues to study pollution-related sources of deterioration to outdoor cultural resources. Towards this end, new studies focusing on biodeterioration will play an important role.



Biological growth on the wall of a structure in Xunantunich, Belize

production of corrosive metabolites that can solubilize minerals in a manner similar to other chemical processes. The role of acids produced by fungi isolated from stone monuments has been demonstrated in the laboratory. However, low frequency isolation cannot be directly correlated with metabolic activities as the fungi isolated in culture media may be dormant and not necessarily the ones functioning in the ecosystem.

The contribution of lichens in stone degradation is fairly well established. They cause chemical damage through the production of biogenic acids and physical damage through the penetration of their rhizine/hyphae into stone fissures.

Most microorganisms involved in bio-decay of monuments produce organic acids, which have been discussed in the scientific literature as a permanent cause of biodeterioration. However, their suggested role has not been proven conclusively. There is an apparent lack of research to assess the susceptibility of a wide range of stone types to microbial deterioration. In instances where several types of microorganisms are present, it is difficult to assess to what extent each one is detrimental to the stone. Also, for all microorganisms the quantitative aspect has been the primary basis for evaluating their importance in the biodeterioration processes. But the level of the normal environmental biological populations — above which these microorganisms could become pathogenic for stone monuments — is yet to be established in the field. It is clear that further research is required to fully understand the extent and the role of these metabolites.

Another important question is the interaction between microorganisms and air pollutants such as sulfur dioxide, nitrogen oxides and particulate matters, and their combined contributing role, if any, in the bio-decay of stone.

Combating biodeterioration problems

Several accounts of biocidal treatments are available. Some have been based on cultures in the laboratory, but most have been based on field trials. There is a lack of published information on their relative effectiveness over an extended period. Periodic qualitative and quantitative monitoring has not been considered vital in assessing the efficacy of biocides on substrata. In practice, visual observations of the appearance of microorganisms on monuments have been the sole method for evaluating the long-term effectiveness of biocides.

Biocides for treating cultural properties usually are selected for their apparent successful use elsewhere on different materials, their availability and their affordability. Most of the evaluation tests have been based on trial-and-error in the field.

Attention has not been given to identifying appropriate biocides based on their molecular structural-activity relationship properties. Product testing currently relies heavily on information provided by the manufacturers, and there is a great need for thorough independent study of compounds considered for use as biocides. Such research may eliminate inappropriate selection of biocides for testing or use.

Most research on biocides has focused on eliminating algae, lichens, fungi, mosses, liverworts and higher plants. Despite the extensive work on the role of bacteria in stone decay, relatively little research has been conducted on antibacterial treatments for stone. Possible antibacterial treatments need further research.

A good residual biocide that would deposit a long-term reservoir of the appropriate chemical in and on the stone substrate has not been identified. Research is required to identify such

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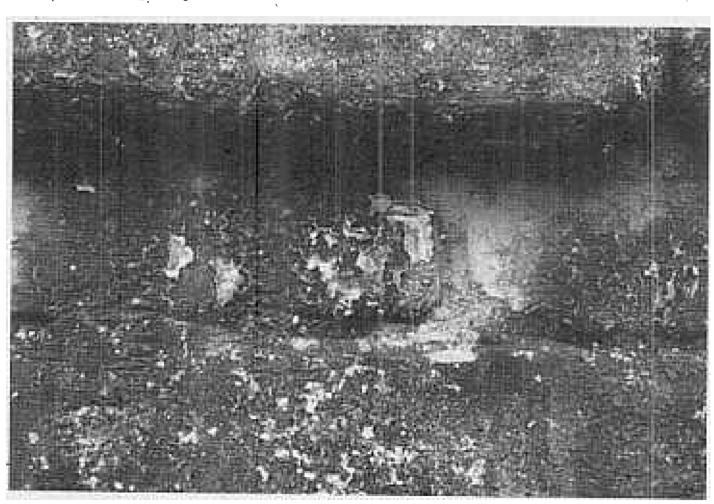
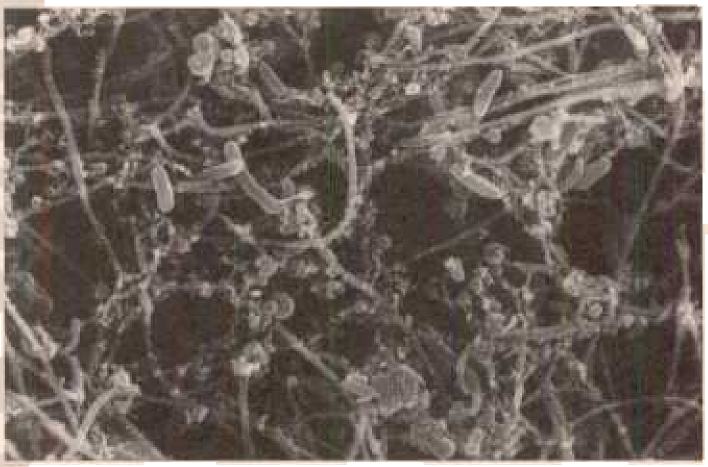
Close up of a biologically deteriorated stone surface, due to black algal growth





*A scanning electron micrograph shows a **biofilm of micro-organisms** magnified 5,600 times*

Biotechnology and preservation

During the past twenty years, the field of molecular biology has revolutionized biology. New techniques have spawned a wide range of technologies with applications in medicine, agriculture and the production of industrial chemicals. In October 1997, a three-day course was held in Turin, Italy, sponsored by the Italian Foundation for Biotechnology. The purpose was to teach preservationists about the role biotechnology could play in the preservation of cultural materials. Participants, mostly conservation scientists, were drawn from Italy and other parts of Europe. The teaching faculty came from five countries.

The course was divided into four sections: deterioration, methods of analysis, restoration and conservation, and the use of biocides. I introduced the first topic with discussion of the role of microbial biofilms in the degradation and discoloration of materials. I explained how biofilms were responsible for damage to stone, paintings, frescoes and manuscripts. Dr. F. Eckhardt from the University of Kiel, Germany, explained the relationship between the molecular composition of the materials and the activity of the micro-flora. The organisms may cause damage over long periods of time, working slowly on the material because of nutritional deficiencies.

Air pollution effects were described by Dr. C. Lalli from Florence, Italy and Dr. C. Saiz-Jimenez from Siviglia, Spain. They described how airborne organic and inorganic pollutants deposit on buildings and monuments, particularly in areas protected from rain. Both acid rain and hydrocarbons provide rich sources of nutrients for bacteria, and interaction between chemical pollutants and microflora is responsible for building deterioration.

In the section of the course devoted to analytic methods, Dr. O. Salvadori from Venice, Italy reported on her research in which both adenosine triphosphate and dehydrogenase activity yield very accurate measurements of microbial activity. Dr. S. Roelleke, a molecular biologist from the University of Vienna, Austria, explained how modern molecular methods permit accurate identification of bacteria on cultural materials. Even extremely small numbers of bacteria or those that cannot be identified by conventional taxonomic methods can be defined by using polymerase chain reactions and other recently-developed molecular methods.

The presentations demonstrated how biotechnology is having an important impact on restoration and conservation methods. Dr. C. Sorlini, from the University of Milan, Italy described recent research in which bacteria were successfully inoculated to calcareous stone materials to remove sulfates and nitrates. The use of enzymes was described by Dr. P. Cremonesi, a conservation chemist from Milan. Dr. Cremonesi has used enzymes throughout Europe to clean paintings and manuscripts. It seems likely that in the near future both bacterial cultures and purified enzymes will be used extensively in conservation.

The use of biocides was discussed by a number of participants. Industrial biotechnology appears to be yielding new longer-lasting and environmentally acceptable biocides. We are also beginning to see the use of biosensors to determine the extent of biodeterioration of stone materials. One of the course participants, Dr. R. D. Wakefield, from the University of Aberdeen, Scotland, described the use of a new laser-based biosensor capable of detecting the effectiveness of biocides in the protection of stone, including a hand-held biosensor that can be used effectively in the field.

This course clearly demonstrated that biotechnology has arrived in the field of conservation. Biotechnology has much to offer in the preservation of cultural material. Transferring information gained in biotechnology to conservation is the challenge in years to come. Substantial interaction between microbiologists and conservationists was an important first step.

—Ralph Mitchell

Dr. Mitchell, the Gordon McKay Professor at Harvard University, is concerned primarily with environmental microbiology and particularly the effects of pollutants on stone. Dr. Mitchell, in cooperation with the National Park Service, is studying the interaction between air pollutants and microbes causing degradation of historic buildings and monuments.

Concrete degradation: Is there a new slice of the pie we should worry about?

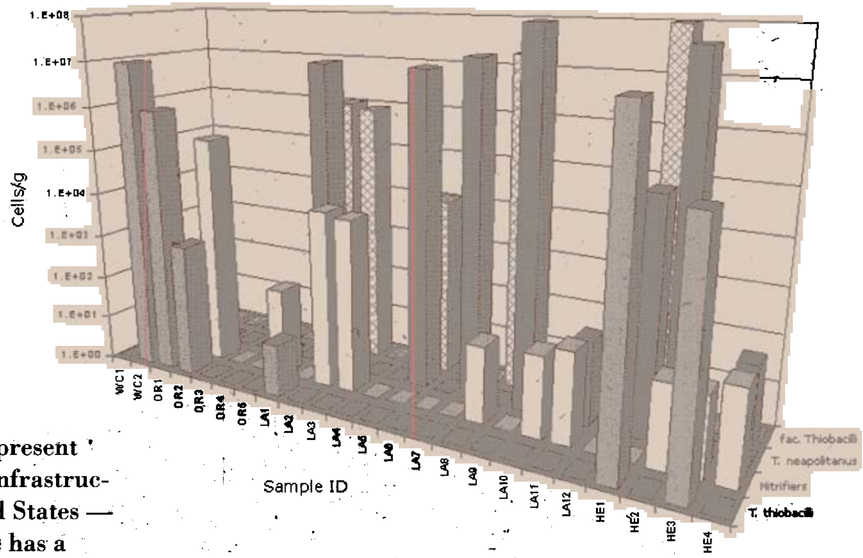


Figure 2—Quantities of MID bacterial species typical of those found on samples of degrading concrete

Concrete is among the world's most heavily consumed substances, with approximately six billion tons produced every year. Concrete has an aura of indestructibility, stemming partly from its rock-hard solidity, the survival of some ancient concrete structures, and the industry slogan of "concrete for permanence." Notably, many structures with concretes based on portland cement have been in service for over 100 years. However, if indestructibility were the rule and not the exception, many thousands of ancient concrete structures would still exist. At the present time, the failing infrastructure of the United States — in which concrete has a prominent role — and the degradation of historically significant structures provide reliable evidence that concretes are fallible under pressures of use and environment.

Microbial activity

In general, the public does not have a clear sense of the catalytic role that microorganisms have in perpetuating environmental change. While microorganisms are invisible to the unaided eye (averaging one to two microns in size), their activities are abundantly apparent.

Microorganisms' appetite for processing organic and inorganic materials is enormous. They are responsible for the purification of millions of liters of raw sewage, the yearly production of 20 billion metric tons of the "greenhouse" gas carbon dioxide, and the extraction of nearly 25 percent of the copper recovered from copper ore. But there is little public appreciation for significant adverse economic impacts of microbial activity on man-made materials. Microbial activity has been shown to be responsible for tens of billions of dollars of damage to structures, materials exposed to aquatic conditions, buried pipe, and historically significant buildings and artifacts.

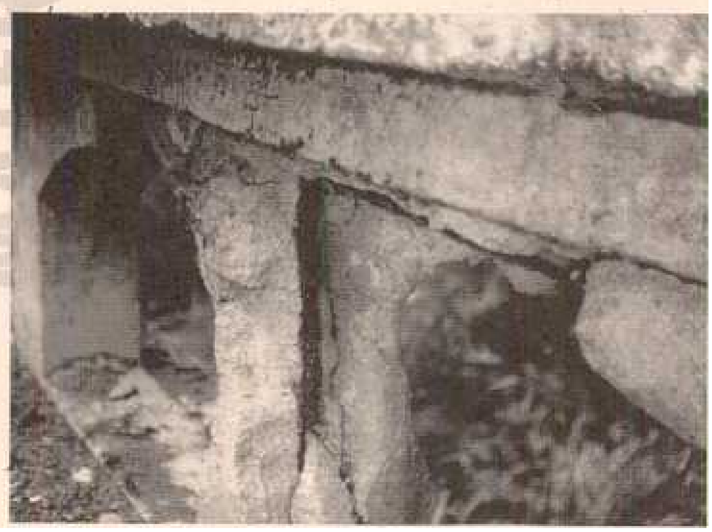


Figure 1—Deteriorating section of a concrete bridge (detail)

Microbially influenced degradation

What is the outcome when the "durability" of concrete meets the determination of microbial activity? Does the outcome follow the adage of the immovable object meeting the irresistible force?

As preface to answering to these questions, reference should be made to the chemical and physical processes commonly accepted as causes of concrete degradation. There are at least seven physical/chemical contributors that promote concrete degradation. These slices of the degradation pie include sulfate and chloride attack (de-icing salts, sea water, sulfur and nitrogen pollutants), alkali aggregate reactions, water leaching, freeze/thaw cycling, salt crystallization.

But the pie will be incomplete without a biological slice known as microbially influenced degradation. And rather than asking if MID is important, it is more appropriate to inquire how big is this slice of the pie.

Initially, MID effects were associated chiefly with the rapid degradation of concrete in major sewer systems. Interest in MID effects was sparked by a bus falling into a sink hole developed in a degrading concrete sewer main. Unfortunately, because of the interest in sewer damage, little concern has been given to the effect of MID on massive above-ground structures. But degradation of massive concrete structures does occur (Figure 1).

Armed with this knowledge, a study was conducted to detect the presence of MID microorganisms at degradation sites. Samples were taken at sites on concrete bridges and other structures. From extensive analysis, MID microorganisms were found at a high percentage of areas of destruction (Figure 2). These data were most interesting and resulted in a quandary: Were MID microorganisms present as a result of degradation or as promoters of degradation? If the latter is correct, then it is fair to ask where these microorganisms obtain the necessary nutrients to survive and degrade solid concrete? The answer to this question is at the center of a new scientific inquiry.

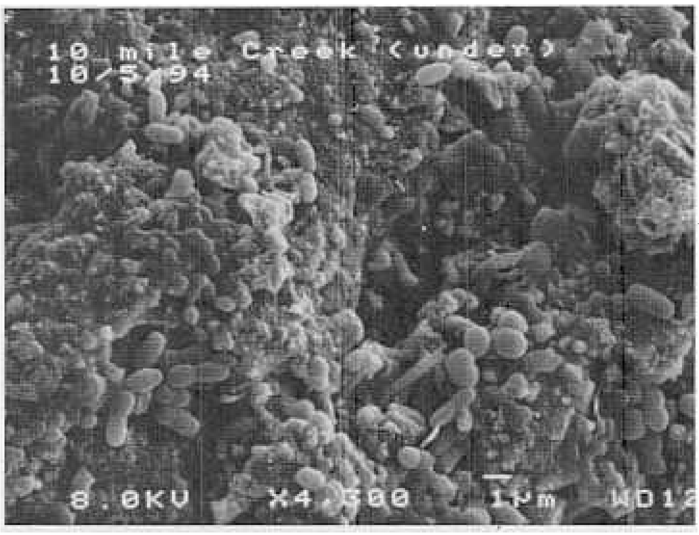


Figure 3—Electron micrograph of deteriorating concrete surface showing microorganisms; note that bacteria are held to the surface by biofilm adherence

Mechanism of MID

Microbially-induced degradation of concrete occurs when ubiquitous, environmental microorganisms produce organic and inorganic acids that dissolve and disintegrate the concrete matrix. This is not, however, a process similar to a one-time application of acid to a concrete surface. The action is intensified because the continued acid release by the microorganism at the site of attack greatly magnifies its intensity. In essence, the microorganisms act as micro-point sources for continuing acid application.

Three groups of bacteria and some fungal species have been implicated in actively promoting MID. Bacterial groups include sulfur-oxidizing bacteria (SOBs), nitrifying bacteria, and some organic-acid-producing bacteria. SOBs most often are associated with aggressive MID of concrete. SOBs identified in concrete attack belong to the genus *Thiobacillus*, which obtain their energy by oxidizing reduced, inorganic sulfur sources such as elemental sulfur, thiosulfate and, importantly, hydrogen sulfide, sulfur dioxide, and sulfite into highly corrosive sulfuric acid. No evidence yet exists to suggest that microbes produce enzymes that allow them to "eat and digest" concrete.

Significance of environmental sources of sulfur to MID

Sulfur in the atmosphere is continually replenished through natural and anthropogenic sources. Prevalent among the natural sources are volcanoes and sea spray. Anthropogenic releases result from the burning and processing of fossil fuels, recovery of metals from metal sulfides, steel production, and pulp and paper processing. Major sulfur species derived from these sources include sulfur dioxide and hydrogen sulfide. The concern over these species is that they can transform into sulfuric acid in the atmosphere or on collecting surfaces.

It is known that sulfur pollutants have a finite half-life on environmental surfaces such as stone and concrete. SOBs are an overlooked catalyst in the oxidation of these pollutants. Recent evidence suggests that these organisms can convert sulfur dioxide and sulfite into sulfuric acid on the surface of inorganic material. The bacteria reside on the surface in a self-made sticky sleeping bag of biofilm (Figure 3). This substance protects them from harmful environments while at the same time allowing the circulation of essential air, water, and sulfur compounds. Because sulfur pollutants, either in a gaseous form or dissolved in water have free movement within the biofilm, they become ready sources of food. Activity of the individual bacterium results in the production of microsites of highly concentrated sulfuric acid that becomes trapped against the surface of the concrete. The resulting reaction causes a loss of binding materials and a subsequent softening of the surface. As the deteriorating surface sloughs away, a fresh surface is provided for biofilm attachment. This process is repeated endless times until mineral removal becomes detrimental to concrete stability.

It can be said with certainty that MID is an important part of the concrete degradation pie — a

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AAM's Museum Assessment Program

The American Association of Museum's Museum Assessment Program has set the following application deadlines for 1998 MAP/Institute for Museum and Library Services grants—

April 24	MAP I	Institutional Assessment
March 13	MAP II	Collections Management Assessment
February 27	MAP III	Public Dimension Assessment

More than 3,000 museums, including the majority of those recently accredited by AAM, have used the Museum Assessment Program as an efficient and effective means of ensuring that their institutions are operating well. The MAP process can enhance a museum's ability to develop its audience, define its mission and vision, set priorities for change and care for collections.

In fiscal year 1997, IMLS awarded 223 museums MAP grants totalling nearly $445,000. Grants for first-time participants in each MAP category are available through IMLS; museums also can pay to participate in the MAP program.

For further information on the 1998 MAP program — including application forms — contact Barbara Ballentine at AAM/MAP, 1575 I Street NW, Suite 400, Washington, DC 20005; telephone 202/289-9119, facsimile 202/289-6578.

US/ICOMOS 1998 International Summer Internships

Applications for the United States Committee of the International Council on Monuments and Sites' 1998 international summer internships are due March 9, 1998.

Each year, US/ICOMOS sponsors paid internships for graduate students and young professionals — 22-35 years of age — throughout the world. Participants work for public and private non-profit historic preservation organizations and agencies under the direction of professionals. Disciplines represented in the US/ICOMOS program include historic architecture, historic landscapes, materials conservation, history and interpretation, archeology, and museology. US/ICOMOS internships generally last three months.

The internships are supported by US/ICOMOS in partnership with a broad range of preservation and conservation organizations and institutions, including NCPTT. Since 1995, NCPTT has sponsored 14 internships (reported in *Notes* 7, 15 and 19); NCPTT's sponsorship will continue in 1998.

For further information on US/ICOMOS' 1998 international summer internships program — including application forms — contact Ellen Delage at US/ICOMOS, 401 F Street NW, Washington, DC 20001-2728; telephone 202/842-1866, facsimile 202/842-1861.

Alicia Trissler joins NCPTT

NCPTT announces the appointment of Alicia Trissler as an MRP Associate. Alicia holds an educational specialist degree in Educational Technology and a master of arts in History/Cultural Resource Management from Northwestern State University. Using her computer and research skills, Alicia is organizing an extensive bibliographical database pertaining to acid rain research that will be added to the NCPTT Web site. She is also organizing and creating a filing system for 16 years of paperwork generated by the National Park Service's Acid Rain Program. Prior to joining NCPTT, Alicia worked with the National Park Service's Southeastern Archeology Center as an archeologist at Oakland Plantation in Natchitoches Parish, Louisiana.

Concrete degradation

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recognized degradation process known to adversely affect concrete integrity.

In order for MID to be recognized as a process that adversely affects the durability of massive concrete structures, it will be necessary to link the occurrence of environmental sulfur pollutants with MID activity. Efforts to do this are underway. A collaboration is being forged among those having information on sulfur pollutant transport and surface absorption, concrete and stone degradation, and microbial surface activity. It is hoped that research will show how significant the MID piece of the pie is. Different environments appear to have a tendency to promote different responses, and it is possible that there is a synergism that results in cumulative effects from physical/chemical and biological processes.

—Robert D. Rogers
Melinda A. Hamilton
Lee O. Nelson

Dr. Rogers, Dr. Hamilton and Mr. Nelson are associated with the Biotechnology Group at the Idaho National Engineering and Environmental Laboratory. One of Dr. Rogers' areas of expertise is the development of microbiological processes for direct environmental application. Dr. Hamilton's work has centered on microbial influenced degradation of concrete and phytoremediation. Nelson's area of interest is in physical and chemical transformations in inorganic materials including concrete and sulfur.

Biodeterioration of stone: What do we know?

Continued from page 3

systems within the established criteria of biocides selection for combating the biodeterioration of stone monuments and sculpture. For example, in areas of heavy rainfall, the development of effective residual compounds such as copper- and zinc-based biocides could be very useful. This would limit the possibility of biocide loss, thereby prolonging the time between re-applications.

No biocide has been found that is uniformly effective on all organisms and on all stone substrates. Further research is needed on biocidal treatments on different stone substrates within the framework of other conservation treatments — in order to avoid interaction with conservation materials prior or subsequent to biocide application. The use of biocidal solutions may introduce chemicals into the substrate that can result in formation of soluble salts and initiate salt crystallization damage. Recent studies indicate that the materials commonly used for water-repellent treatments or stone consolidation may increase the potential for biological growth by providing nutrients for microorganisms. This possibility also needs to be considered in studying biocides.

Little effort has been made to investigate the merits of traditional techniques, such as using natural products for their biocidal properties. In tropical environments this may prove to be a more viable and cost-effective solution than the use of expensive chemicals and synthetic products that may be toxic to humans and hazardous to the environment.

The author's own extensive survey of published biodeterioration literature suggests that the problem as it relates to historic preservation currently is under-researched. Many of the works published to date are largely empirical in nature and have yet to be adequately substantiated by long-term experimentation.

Biodeterioration research demands an interdisciplinary approach, and the outcome of the study must have field applications. This does not imply that long-term strategic and fundamental research should be discouraged, but that such work ultimately must contribute to the care and preservation of our stone-built cultural heritage.

—Rakesh Kumar

Economic impact of historic preservation

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locally and to possess a wider array of measures that can be used to analyze impacts. In particular, RSRC's model is one of the few regional economic models that enable analysis of government revenue impacts and analysis of gains in total regional wealth.

In the New Jersey study, the PC I-O Model was applied to various aspects of historic preservation that bear on its economic contribution—including historic rehabilitation, heritage tourism, and the operations of historic sites and organizations. Analysis of property taxes paid by historic buildings and how landmark designation enhances property values also was undertaken. Impacts are given for the latest years for which complete information was available at the time of analysis and include direct and multiplier effects. The results are summarized in the table on page nine.

The total annual direct economic impacts of historic preservation in New Jersey includes $123 million in historic rehabilitation, $432 million in heritage tourism spending, and $25 million in net spending by historic sites and organizations.

When multiplier effects are applied to these direct effects, the total annual impact to the nation is 21,575 jobs, $572 million in income, $929 million in GDP and $415 million in taxes. New Jersey's benefits are 10,140 jobs, $263 million in income, $543 million in GSP, $298 million in taxes and $460 million in in-state wealth. As part of these benefits, New Jersey historic properties pay annually $120 million in property taxes. These estimates of impacts are considered conservative because they do not include the effects of construction on historic properties that are eligible for the National Register of Historic Places but are not yet listed.

Testing concludes that the economic benefits of historic preservation — such as total job creation, increased income and GDP per $1 million invested — surpass those of other investments such as new housing or new commercial construction. It is clear from this study that, given the powerful economic pump-priming effect of historic preservation including its considerable tax benefits, public programs to foster preservation can realize sizable economic development gains often at little or no cost to the taxpayer. New Jersey Historic Trust itself is a good example of such gains. By mid-1997, New Jersey Historic Trust had awarded approximately $55 million in grants for historic rehabilitation. This sum will leverage approximately $403 million of private and other funds for preservation and rehabilitation.

This article summarizes a report to the New Jersey Historic Trust by the Regional Science Research Corporation of Rutgers University. The project was supported by NCPTT's 1995 PTTGrants program. Copies of the report (NCPTT Publications No. 97-05) are available from Mark Gilberg, NCPTT Research Coordinator.